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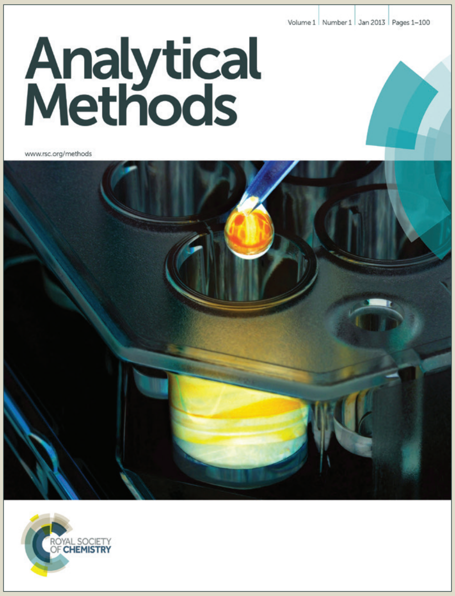

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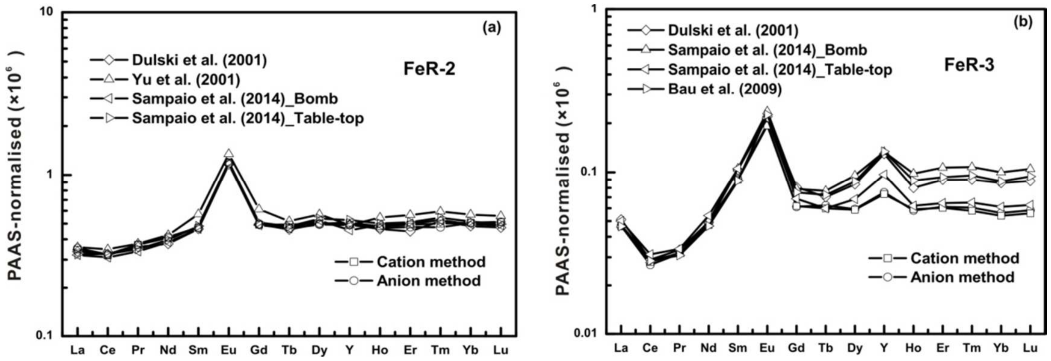

Comparison between the REE data of this work and literature values by Yu ZS *et al.*, Sampaio *et al.*, Dulski *et al.*, and Bau *et al.* in reference materials FER-2 (a) and FER-3 (b) using PAAS-normalized REE patterns.

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ARTICLE TYPE

Analysis of ultra-low level Rare Earth Elements in magnetite samples from banded iron formations using HR-ICP-MS after chemical separation

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Abstract

We have investigated two methods for the separation of rare earth elements (REEs) and Fe in magnetites from banded iron formations (BIFs), employing cation- and anion-exchange chromatography. The separated REEs were subsequently determined using a high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS). Our results indicated that 10 mL concentrated HCl was sufficient to completely separate all REES from Fe using anion exchange chromatography, whereas more than 30 mL 6 mol L^{-1} HCl was required using cation-exchange. The recovery of REEs using both methods was 100% ± 5%. The procedure blanks varied from 0.029 ng g^{-1} for La to 0.018 ng g^{-1} for Lu in anion exchange, and from 0.151 ng g^{-1} (again check your figure of significance) for La to 0.031 ng g^{-1} for Lu in cation exchange, respectively. Our results indicated that anion exchange method has advantages over cation exchange for the analysis of ultra-low level REEs in magnetites. The proposed methods were tested using the reference material FER-2.

Introduction

Banded iron formations (BIFs) are distinctive sedimentary rocks, having alternate layers of iron-rich minerals and chert[1, 2].Presently, BIFs have caught the attention of scientists, who have conducted more researches on the fields of geochemistry and ore deposit geology. The BIFs provide a comprehensive insight into major changes that triggered the evolution of Earth, and also hold significance as the main type of iron resources. BIFs commonly contain rare earth elements (REEs), including yttrium (Y-39), which can be useful in elucidating the chemical composition, oxidation state of ancient seawater and the atmospheric changes on land [3].

Whole-rock geochemical analysis[4, 5] of BIFs, which puts chert and iron bands together as a single sample for analysis, is the most widely used technique for obtaining contents of the REEs. Moreover, some studies [6, 7] have tried to analyze the REEs of chert-rich and iron-rich individual bands, respectively. In fact, there are some invisible micro-banding within a single chert-rich or iron-rich lamination, pure chert and iron bands cannot be completely separated from the bulk sample by simple physical separation methods[8]. And these studies only provide information about mixing products of various minerals. Therefore, in order to well constrain the origin of iron, researches have to extensively focus on analyzing REEs of magnetite separated from the BIFs. Due to the large amounts of iron trace amounts of REEs in most BIFs samples (normally sub ng g^{-1}), very few studies have reported the determination of REEs in magnetite from the BIFs [9]. Yang *et al.*[9] conducted chemical analysis of magnetite samples to determine the REE contents. The contents of REEs in their magnetite samples were at the μg g^{-1} level, and the study did not provide sufficient uncertainty for the concentrations of REEs. In addition, an *in-situ* analysis technique for determination of REEs is performed on magnetite samples of BIFs using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)[10, 11]. However, this method has relatively great detection limits at the order ranging from μg g^{-1} to sub μg g^{-1} [12, 13]. To date, no study has reported the content of REEs at the level of ng g^{-1} in magnetite samples from BIFs.

Inductively coupled plasma mass spectrometry (ICP-MS) is considered to be an ideal tool for determination of REEs, owing to its multi-element capability, low detection limits and high sample throughput[14, 15]. However, there are still some drawbacks of this technique, such as progressive clogging effects at the interface, which are quite pronounced as the sampling process involves the use of physical plasma. Other notable drawbacks of this technique include the drift phenomena, various interferences, and matrix effects, especially at low concentration levels. For the studied magnetite samples, iron is the only major component and the Fe ions are heavier than Ar ions[16], so the accuracy of the analysis is severely hampered by iron matrix effects. In additon, in the case of iron-rich samples, the detection limit of ICP-MS is generally poorer by 2–3 orders of magnitude [17].

In several studies, different kinds of analytical methods and adjustments have been reported to overcome matrix effects that hinder the accurate determination of REEs at low concentration. Isotope dilution mass spectrometry[18] is one such analytical technique that is widely known for its high precision and effectiveness in correcting instrument drift and matrix effects. However, the limitation of this method is its inability in determining monoisotopic REEs (^{141}Pr, ^{159}Tb, ^{165}Ho, and ^{169}Tm). Moreover, this method is time-consuming and relatively expensive. When flow injection (FI) sample introduction system coupled with ICP-MS, the matrix effects are partially overcome[19]. This arrangement does not ensure the accurate determination of REEs in magnetite samples. Additionally, the precision of results is easily affected by fluctuations in the pumping rate of the peristaltic pump[20]. Therefore, chemical methods are commonly used for carrying out routine enrichment of REEs in analytical solutions. HF co-precipitation is an effective separation technique by which the entire group of REEs can be precipitated out in the form of fluoride residue[21]. $Fe(OH)_3$ is also used to scavenge the REEs[22,23]. While performing HF co-precipitation, several precautionary measures need to be taken as these chemicals, especially HF are hazardous to bones. Nevertheless, Qi *et al.*[24] described an inorganic co-precipitation method to pre-concentrate REEs. Chromatographic separation methods are quite effective in separating and enriching REEs from coexisting elements, which are at extremely high concentrations in sample solutions[25]. In general, cation-exchange chromatography is used to carry out low-level analysis of REEs[26,27], whereas anion-exchange chromatography is often applied to the fields of Fe[28], Lu-Hf [29], and Re-Os isotope system[30]. In this study, we used both types of ion-exchange chromatography to separate REEs from the matrix Fe for magnetite samples of BIFs. These chromatographic techniques were found to be compatible with the ICP-MS procedure. The potential of these two chromatographic methods were then evaluated by performing the analysis of reference materials from the BIFs (FER-2, FER-3). We thoroughly investigate and compared the efficacy of cation and anion exchange methods in separating ultra-low levels of REEs from magnetite samples of BIFs. Once developed, these methods will be used for performing low-level analysis of REEs on a suite of iron-bearing minerals, such as pyrite, hematite, and siderite.

Experiment

Instrumentation

A Thermo Fisher Scientific Element I ICP-MS at the Institute of Geology and Geophysics, Chinese Academy of Sciences in Beijing, China was employed for this study. The components of the sample introduction system, namely, the nebulizer spray chamber, torch, and the cones were cleaned before use.

The sensitivity of this instrument was adjusted to 1.5×10^6 counts per second (cps) in order to achieve the expected detection limit of 1 ppb for ^{115}In. The oxide formation level of CeO relative to Ce was routinely maintained at lower than 2‰. The sample holding component was washed for 1 minute using 3% *v*/*v* HNO_3 before introducing every sample. The details of the instrumental operating conditions and measurement parameters were summarized in Table 1.

Table 1
Summary of operating conditions for ICP-MS measurements

The calibration was performed using four working standard solutions of REEs, having concentrations of 0.1, 0.5, 1, 5 ng g^{-1}, respectively and a blank solution in 2% *v*/*v* HNO_3. In order to correct the instrumental drift, the internal standard concentration of In was maintained constant at 2 ng g^{-1} in the sample solutions, calibrators, and blank solutions.

Reagents and Samples

Ultra-pure water with a resistivity of 18.2 MΩ cm^{-1} was obtained from a Milli-Q water purification system. Concentrated nitric (HNO_3), hydrofluoric (HF), and hydrochloric acids (HCl) (GR grade, 10mol L^{-1}) were purified by performing sub-boiling distillation in PTFE distillers. Hydrobromic acid (HBr) (GR grade) was purified by sub-boiling distillation in a quartz still. The strongly acidic cation-exchange resin AG50-X12 (200-400 mesh) and anion-exchange resin AG1-X8 (200-400 mesh) were obtained from Bio-Rad (Richmond, CA,USA).

An eight-step serial gravimetric dilution scheme was used to prepare external calibrators and required concentrations of REEs from mixed multi-element certified solutions (SPEX CertiPrep, NJ, USA) containing 10 μg g^{-1} of all REEs. To prepare stock iron solutions of different concentrations, highly pure magnetite sample (99.99%) was dissolved and diluted appropriately.

Three magnetite samples were supplied by the Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing, China. These magnetite samples were collected from the typical BIFs that were found in Henan province of China. In this study, we selected two reference materials of iron formation (FER-2, FER-3) because we could not find a single magnetite reference material that could exactly match with the samples. Although the studied samples and reference materials were related to BIFs, there were significant differences in the iron contents present in the studied samples and reference materials.

Sample Preparation

About 100 mg of reference materials and studied samples were weighted accurately into the 15 ml round-bottom Savillex^{TM} Teflon screw-cap capsules. 1 ml of HF and 2 ml of HBr were added to the Teflon capsule to dissolve the reference materials and samples. Finally, the Teflon capsule was heated to a temperature of 130 °C on a hot plate for 48 h.

After achieving complete dissolution of each sample, the capsule was opened and the sample was evaporated to fumes at 140 °C. The capsule was sealed at room temperature prior to chemical separation.

The separation procedure was as follows:

(1) Cation exchange resin AG50W-X12 separation (“cation

method")

1 mL of 6 mol L^{-1} HCl was added to the residue and dried. After cooling this dried residue, it was dissolved in 1 ml of 2.5 mol L^{-1} HCl. The capsule was sealed overnight on a hot plate. After cooling, the content of capsule was loaded on a quartz column packed with a 2 mL resin bed of AG50W-X12 (200-400 mesh)[31] which was pre-conditioned with 2 mL 2.5 mol L^{-1} HCl. To remove the bulk matrix elements (major elements), the column was eluted with 10 mL 2.5 mol L^{-1} HCl. The REEs were eluted with 30 ml of 6mol L^{-1} HCl. The eluate of REEs was gently evaporated and dissolved in 10 mL 2% HNO_3 solution containing 2 ng g^{-1} In.

(2) Anion resin AG1-X8 separation (here defined as the "anion method")

The residue was dissolved in 10 mol L^{-1} HCl. This concentrated HCl was used as the eluent.. The AG1-X8 resin[32] was pre-cleaned and pre-conditioned using 10 mL concentrated HCl before sample loading. After loading these sample solutions onto the resin, REEs were eluted using 10 mL concentrated HCl. Then, the eluate of REEs was dried down and dissolved in 10 mL 2% HNO_3 solution containing 2 ng g^{-1} In.

Results and discussion

REEs purification and recovery rate of REEs

The suitabilities of AG50W-X12 and AG1-X8 resins were initially tested by loading the prepared solution. The prepared solution was mixed with 5 ng g^{-1} REEs standard solution so that the iron concentration in the solution was 150 mg g^{-1}. This equivalent concentration of iron was consisted with the studied magnetite samples.

Cation method:

The elution profile depicted the measurements of REEs and Fe on cation resin in HCl media. First, the prepared solution was loaded onto the resin. Thereafter, 2.5 mol L^{-1} HCl was added onto the resin to effectively remove 99% of matrix Fe element. This could be achieved because Fe was loosely adsorbed onto the cation resin (fig.1). REEs having the highest affinity for cation-exchange resin were recovered by using 6 mol L^{-1} HCl solution as the eluting agent. The distribution coefficients of REEs determined the sequence in which the REEs were stripped from the resin column. When 6 mol L^{-1} HCl solution was loaded onto the column, heavy REEs (HREE) were stripped from the resin column first, followed by middle REEs (MREE) and light REEs (LREE) (fig.1a, b, c). LREE were the most difficult elements to be eluted out from the resin column. We found that at least 30 mL of 6 mol L^{-1} HCl was required to obtain high recovery (more than 95% for each) of REEs (fig. 2a).

Fig. 1 Elution profile of REEs and iron when AG50W-X12 cation exchange resin was used. The prepared solution contained 5 ng REEs and the equivalent of 150 mg iron to simulate the magnetite. Concentrations of REEs were determined by ICP-MS. (a) Elution curves of HREE by 6 mol L^{-1} HCl (including Y, Ho, Er, Tm, Yb, Lu); (b) Elution curves of MREE using 6 mol L^{-1} HCl (including Sm, Eu, Gd, Tb, Dy); (c) Elution curves of LREE using 6 mol L^{-1} HCl (including La, Ce, Pr, Nd).

Fig. 2 The recoveries for the both cation method (a) and the anion method (b). The recoveries were calculated from the counts per second (cps) of prepared solution divided by cps of the 5 ng REEs standard solution without any Fe.

Anion method:

Cations did not interact with the anion exchange resin. So, when HCl media was used as the eluent, REEs rapidly passed through the anion resin column without any fractionation. The matrix Fe in HCl medium was converted into $FeCl_4^-$ complex. In fact, the anion resin's adsorption capacity of Fe was related to the concentration of HCl. While performing the analysis of magnetite samples, the adsorption capacity of Fe was visible because the color of the resin's column changed after the sample solution was loaded onto the column. As shown in fig.3, an increase in the concentration of HCl media roughly increased the overall adsorption capacity of Fe in anion resin, except for 6 mol L^{-1} HCl solution. When 6 mol L^{-1} HCl solution was used, the exchange capacity of 1 mL wet resin was approximately 75 mg of Fe, which was in complete agreement with the results reported in a previous study conducted by S. Ronny *et al*. [28]. Therefore, while performing the procedure of iron separation from magnetite samples, concentrated HCl was used as the media. To ensure high recovery of REEs, 10 ml of concentrated HCl was used (fig. 4). Matrix Fe continued to reside in the resin column in the form of $FeCl_4^-$ complex. As shown in Fig.2b, the recoveries of REEs were more than 95%.

Fig. 3 The exchange capacity of Fe per milliliter wet resin in different concentrations of HCl from 4 mol L^{-1} to 10 mol L^{-1} (sub-boiling distillation concentrated HCl).

Fig. 4 Elution profile of REE through AG1-X8 anion exchange resin. The prepared solution contained 5 ng REE and the equivalent of 150 mg iron to simulate the magnetite. Concentrations of REE were determined by ICP-MS.

Procedural blank levels

The instrumental detection limits and the method limits of detection (LOD) for both methods have been reported in Table 2. The instrumental detection limits were calculated as ten times the standard deviation of the ion counts originating from a 2% *v/v* HNO_3 solution containing 2 ng g^{-1} In. Six replicate measurements of ion counts were performed to determine the standard deviation. The method limits of detection were calculated as three times the standard deviation of the six individual procedural blanks after taking into account the sample's dilution factor.

Table 2
Detection limits of REE by ICP-MS for proposed methods

The values of method LOD indicated that LREE were higher than HREE. This was an insignificant issue when compared with analytical precision. The values of method detection limits for cation and anion methods were generally comparable. Blank values of REEs from the cation exchange method were slightly higher than those obtained by the anion exchange method. This discrepancy could be attributed to the different amounts of HCl used in the two ion-exchange methods. In this study, the achieved method LOD of cation exchange technique was much lower than that reported for the analysis of geological samples[33].

In summary, the achieved detection limits were significantly lower than the concentrations of REEs in magnetite samples, thereby indicating that both methods could be conveniently used for performing the analytical procedures.

Analytical results for reference materials

We could not find a single suitable reference material for the magnetite samples. Therefore, FER-2 and FER-3 (CCRMP, Canada) were chosen as iron formation reference materials (RMs) in this study. ICP-MS analyses were performed on the two RMs by these two separation methods for triplicate. In this experiment, the final solutions obtained by dissolving the materials were very clear without any precipitation. The results of the reference materials analyses were summarized in Table 3 and Fig. 5.

Table 3

Comparison of REE data of this work with literature value for FER-2 and FER-3

Fig. 5 Comparison between the REE data of this work and literature values by Yu ZS *et al.*[35], Sampaio *et al.*[36], Dulski *et al.* [34] and Bau *et al.*[37] in reference materials FER-2 (a) and FER-3 (b) using PAAS-normalized REE patterns.

The achieved contents of REEs from FER-2 were in good agreement with the results obtained by these two separation methods. Moreover, they were comparable with the reported values of direct analysis, which was performed without separation and pre-concentration [34-36].

In case of FER-3, the values of LREE obtained by the two methods were consisted with the reported data of Dulski *et al.* [34] and Bau *et al.* [37].When the results of HREE (from the Gd to Lu) obtained from the two separation methods were compared, we found that the values were approximately 40% lower than those reported by Dulski *et al.* [34] and Bau *et al.* [37], but these values were comparable to the values reported by Sampaio *et al.* [36], a study that employed the same table-top procedure as ours. Compared with the bomb method, the table-top procedure could be performed at a lower temperature and pressure. This indicated that the obtained values of HREE varied with the different digestion procedures. Moreover, HREE and LREE may be present in different phases in FER-3. Li *et al*[38] conducted the experiment of table-top procedure (HBr-HF, the method mentioned here) and bomb procedure (HNO_3-HF) for the two iron-rich samples of BIFs, but the results were found to be no differences between two digestion procedures. Therefore, we could infer that the conditions of digestion did not influence the FER-2 and iron-rich samples. This finding for FER-3 would be thoroughly investigated in the future studies.

The standard addition method was conducted to further evaluate the procedural recovery of the REEs from the BIFs samples. Based on the stable results obtained from the table-top method, it was found that the REEs contents of FER-3 were lower than those of FER-2 by an order of magnitude. Taking these facts into consideration, FER-3 was selected for the purpose of analytical testing. In addition, the anion method was selected owing to its numerous advantages, which had been discussed in below.

0 ng, 100 ng, and 200 ng REEs standards were added to 50 mg FER-3 samples. Then, these samples were analyzed by the aforementioned anion method. To determine the recovery of each REE, the analytical results of samples containing 100 ng and 200 ng REEs were obtained by subtracting the free REEs (0 ng REEs was added) sample. Table 4 listed the recovery of each REE. The recoveries for FER-3 using anion method varied from 95% to 104%.

Table 4

REE Recovery (%) of standard addition to FER-3 using anion method separation

Analytical results for magnetite samples

Three unknown magnetite samples collected from BIFs in the Hunan province, China were repeatedly analyzed by the aforementioned methods. The results and more details were summarized in Table 5. The result of REEs from magnetite samples were shown in the Post Archean Average Shale (PAAS) [39] normalized diagram (Fig. 6).

Table 5

Concentrations (in ng g^{-1}) of REE in the magnetite samples using two methods

Fig. 6 PAAS-normalized REE patterns of magnetite samples from BIFs showing positive La, Eu and Y anomalies. The magnetite samples had a composition typical of both seawater and hydrothermal fluids signatures. Data of hydrothermal fluids and modern sea water were from Bau and Dulski[41] and Kelgwin[42], respectively. (C was short for cation method, while A was short for anion method)

The concentrations of REEs in magnetite samples were found to be at ultra-trace levels between ng g^{-1} and sub ng g^{-1}. The total contents of REEs from these three samples varied from 0.3 to 1.1 μg g^{-1}. Eu anomalies with Eu/Eu* varied from 1.76 to 1.97. This indicated that high-temperature hydrothermal activity was involved in the ore-forming process. In addition, samples were characterized by positive La (La/La*=1.12-1.38) and Y (Y/Y*=1.39-1.51) anomalies, which were typical of seawater signatures. However, these samples exhibited slightly distinct patterns from those of typical BIFs samples[40], which was lack of significant depletion of the LREE by the data of Sm_{SN}/Y_{SN}=0.73-1.23. In short, the REEs patterns and element ratios of magnetite samples collected from BIFs of Henan province had signatures of both seawater and hydrothermal fluids. The hydrothermal fluids was a significant component of the magnetite obtained from this area.

Results obtained using the cation and anion exchange methods, respectively, were nearly the same. But anion method was relatively simple and fast, in which less amount of acid was consumed. In addition, the blank readings of the anion-exchange method were much lower than those of the cation-exchange method. Therefore, the anion approach was more appropriate for determining the ultra-trace levels of REEs in magnetite samples.

Conclusions

In this study, we investigated the efficacy of cation- and anion-exchange chromatography in analyzing the magnetite samples from banded iron formations. The results obtained by both cation and anion methods were in complete agreement with each other. The proposed methods were also tested using the reference material FeR-2. Moreover, the anion method was more suitable for analyzing magnetite samples due to three significant advantages: a shorter process, the use of smaller amount of acids, and lower blanks. In conclusion, these two methods were suitable for analyzing ultra low-level REEs of magnetite samples, while the anion method revealed more advantages in separating metal elements from the REEs.

Notes

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Table 1

Summary of operating conditions for ICP-MS measurements

Parameter	Value
Instrument	Element I ICP-MS
Nebulizer	MicroMist 0.2ml min^{-1}
Spray chamber	Scott (double-pass) type, 50ml
RF power	1300 W
Reflected power	$<$2 W
Cooling gas	14.6 l min^{-1}
Auxiliary gas	0.96 l min^{-1}
Sampling gas	0.90 l min^{-1}
Sample uptake rate	200 µl min^{-1}
Sampling Cone	1.1 mm, Ni
Skimming Cone	0.8 mm, Ni
Detection mode	Counting
Wash time	60 s
Dwell time per isotope	100 ms
Calibration	External
Internal standards	^{115}In

Table 2

Detection limits of REE by ICP-MS for proposed methods

Element	Isotope measured	IDL(10s)	LOD(3s)		Procedure blank	
			Cation method	Anion method	Cation method	Anion method
Y	89	0.004	0.083	0.054	0.214	0.015
La	139	0.001	0.120	0.008	0.151	0.029
Ce	140	0.010	0.310	0.005	0.485	0.100
Pr	141	0.001	0.055	0.014	0.051	0.076
Nd	143	0.002	0.038	0.020	0.055	0.032
Sm	147	0.016	0.030	0.020	0.032	0.025
Eu	153	0.018	0.078	0.019	0.029	0.022
Gd	157	0.018	0.088	0.022	0.059	0.035
Tb	159	0.025	0.104	0.025	0.037	0.027
Dy	163	0.010	0.071	0.011	0.048	0.017
Ho	165	0.009	0.093	0.010	0.033	0.010
Er	166	0.003	0.075	0.004	0.040	0.008
Tm	169	0.001	0.091	0.011	0.030	0.012
Yb	172	0.003	0.081	0.023	0.033	0.024
Lu	175	0.002	0.092	0.018	0.031	0.018

Values for IDL(instrumental detection limits) and procedure blank level were in ng mL^{-1}; LOD (method limits of detection) were in ng g^{-1}.

Table 3

Comparison of REE data of this work with literature value for FER-2 and FER-3

Element	FER-2 (µg g^{-1})						FER-3 (µg g^{-1})					
	Cation	Anion	A	B	C	C	Cation	Anion	A	C	C	D
	Mean±1s (n=3)	Mean±1s (n=3)			Mean±1s (n=4)	Mean±1s (n=4)	Mean±1s (n=3)	Mean±1s (n=3)		Mean±1s (n=7)	Mean±1s (n=4)	
Method	Table-top	Table-top	Bomb	Bomb	Bomb	Table-top	Table-top	Table-top	Bomb	Bomb	Table-top	Bomb
La	13.1±0.4	13.4±0.2	12.8	13.6	12.2±0.5	12.3±0.7	1.77±0.06	1.78±0.01	1.94	1.8±0.1	1.9±0.1	1.76
Ce	25.5±0.1	25.8±0.2	26	27.8	24.8±0.9	26±2	2.25±0.07	2.15±0.04	2.32	2.3±0.1	2.5±0.1	2.28
Pr	3.30±0.06	3.31±0.05	3.2	3.35	3.0±0.1	3.1±0.2	0.284±0.023	0.281±0.014	0.296	0.28±0.02	0.30±0.02	0.274
Nd	13.1±0.4	13.2±0.2	12.0	13.6	12.3±0.5	12.7±0.6	1.51±0.15	1.57±0.09	1.58	1.6±0.1	1.73±0.09	1.49
Sm	2.64±0.07	2.65±0.06	2.6	3.20	2.6±0.1	2.7±0.1	0.503±0.025	0.508±0.022	0.58	0.59±0.06	0.59±0.04	0.496
Eu	1.32±0.46	1.30±0.20	1.28	1.48	1.29±0.05	1.32±0.06	0.213±0.005	0.217±0.005	0.242	0.26±0.02	0.236±0.006	0.248
Gd	2.31±0.18	2.32±0.14	2.33	2.88	2.3±0.1	2.39±0.06	0.290±0.013	0.288±0.002	0.38	0.37±0.02	0.322±0.006	0.353
Tb	0.38±0.02	0.36±0.01	0.354	0.398	0.36±0.01	0.37±0.01	0.046±0.003	0.048±0.003	0.054	0.059±0.005	0.046±0.001	0.0557
Dy	2.20±0.15	2.17±0.18	2.20	2.51	2.3±0.1	2.36±0.04	0.258±0.017	0.260±0.012	0.37	0.42±0.4	0.30±0.01	0.385
Y	13.7±0.2	13.2±0.6	13.3	13.2	12.3±0.3	14.2±0.5	1.98±0.10	2.02±0.06	3.5	3.6±0.2	2.61±0.09	3.62
Ho	0.48±0.02	0.47±0.03	0.463	0.545	0.49±0.02	0.50±0.01	0.059±0.004	0.058±0.004	0.08	0.098±0.008	0.062±0.001	0.0889
Er	1.43±0.09	1.38±0.12	1.3	1.64	1.45±0.06	1.48±0.03	0.175±0.011	0.177±0.005	0.26	0.31±0.03	0.187±0.002	0.27
Tm	0.20±0.01	0.19±0.01	0.207	0.237	0.21±0.02	0.217±0.003	0.023±0.001	0.024±0.002	0.036	0.043±0.004	0.026±0.001	0.0382
Yb	1.42±0.03	1.41±0.04	1.35	1.59	1.39±0.08	1.44±0.02	0.152±0.004	0.157±0.008	0.24	0.28±0.03	0.171±0.009	0.246
Lu	0.22±0.01	0.22±0.02	0.203	0.239	0.21±0.01	0.213±0.005	0.024±0.001	0.025±0.002	0.038	0.045±0.004	0.027±0.001	0.0405

A: Dulski *et al.*[34] B: Yu ZS *et al.*[35] C: Sampaio *et al.*[36] D: Bau M. *et al.*[37]

Table 4

REE Recovery (%) of standard addition to FER-3 using anion method separation

	Added (ng)	Measured (ng)	Recovery (%)	Added (ng)	Measured (ng)	Recovery (%)
La	100	98.5	98.5	200	200.3	100.1
Ce	100	98.3	98.3	200	199.8	99.9
Pr	100	103.7	103.7	200	204.5	102.3
Nd	100	98.4	98.4	200	198.2	99.1
Sm	100	99.2	99.2	200	204.0	102.0
Eu	100	98.2	98.2	200	196.6	98.3
Gd	100	100.4	100.4	200	206.6	103.3
Tb	100	98.2	98.2	200	197.1	98.5
Dy	100	102.7	102.7	200	208.1	104.0
Y	100	95.8	95.8	200	190.5	95.2
Ho	100	103.8	103.8	200	206.0	103.0
Er	100	97.4	97.4	200	199.8	99.9
Tm	100	97.8	97.8	200	196.4	98.2
Yb	100	98.3	98.3	200	205.8	102.9
Lu	100	97.4	97.4	200	196.0	98.0

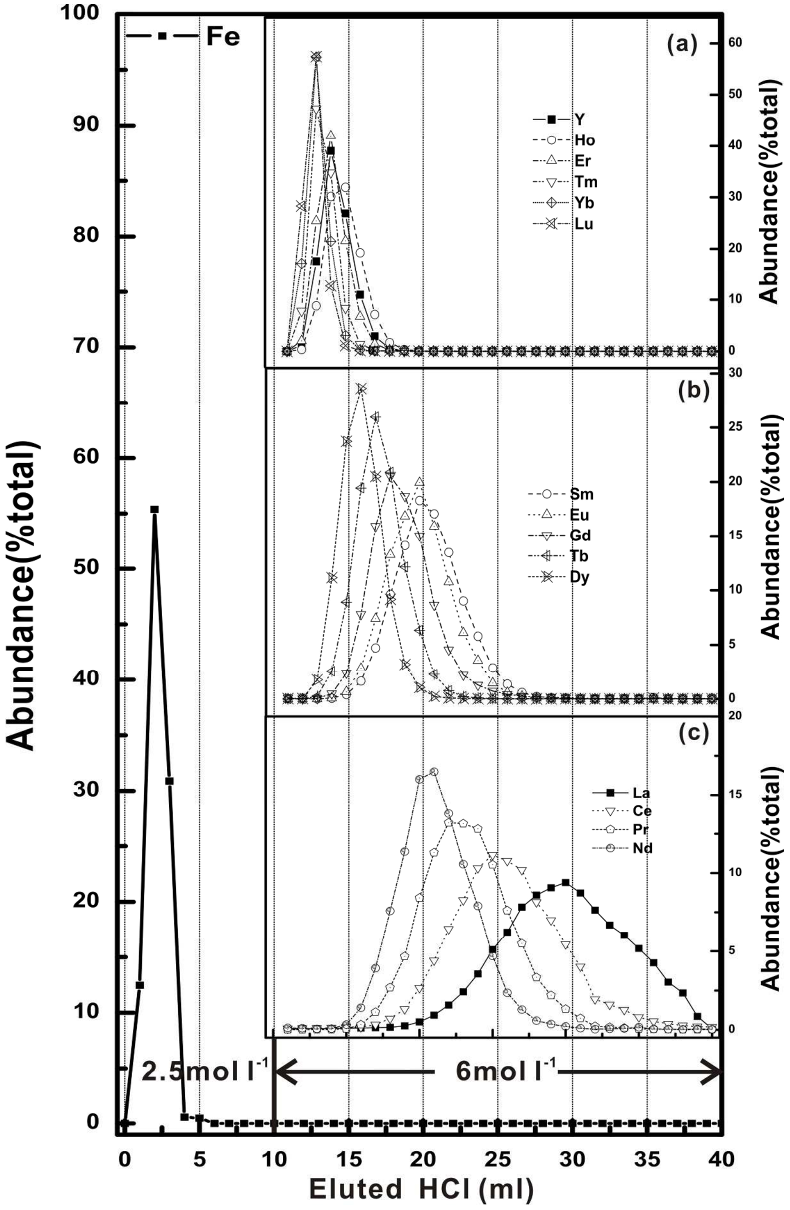
Table 5

Concentrations (in ng g^{-1}) of REE in the magnetite samples using two methods

Element	**SM-1**		**SM-2**		**SM-3**	
	Cation Mean±1s	Anion Mean±1s	Cation Mean±1s	Anion Mean±1s	Cation Mean±1s	Anion Mean±1s
La	80.8±4.6	75.2±3.8	88.3±5.2	93.7±6.3	199±7	202±8
Ce	119±5	126±6	135±6	141±6	357±8	361±9
Pr	12.3±0.9	13.0±1.2	12.9±0.6	13.8±0.8	37.23±2.1	38.12±2.5
Nd	41.6±3.6	44.4±4.2	41.5±3.2	43.0±2.8	127±5	129±6
Sm	7.07±0.52	7.41±0.46	6.51±0.32	6.86±0.40	21.0±1.3	20.9±1.1
Eu	2.73±0.28	2.94±0.32	2.44±0.24	2.55±0.17	7.74±0.62	7.79±0.53
Gd	7.27±0.52	7.65±0.48	6.62±0.62	6.92±0.75	23.1±1.4	23.4±0.8
Tb	1.05±0.02	1.09±0.03	0.83±0.04	0.87±0.05	3.46±0.08	3.50±0.06
Dy	6.48±0.38	6.79±0.46	5.50±0.52	5.90±0.40	22.7±1.9	23.2±2.1
Y	58.4±5.6	60.3±4.9	46.7±7.2	50.7±6.3	211±12	217±16
Ho	1.43±0.12	1.51±0.15	1.24±0.08	1.31±0.13	5.37±0.18	5.39±0.09
Er	3.67±0.18	3.87±0.23	3.08±0.26	3.19±0.19	16.6±0.8	16.2±0.7
Tm	0.50±0.06	0.52±0.05	0.41±0.06	0.41±0.08	2.20±0.12	2.15±0.15
Yb	3.47±0.12	3.55±0.15	2.84±0.12	2.79±0.15	14.4±0.38	14.3±0.42
Lu	0.547±0.036	0.562±0.038	0.452±0.021	0.447±0.018	2.16±0.21	2.05±0.26
∑REE	346	355	354	373	1049	1066
Eu/Eu*	1.92	1.97	1.92	1.91	1.76	1.77
Y/Y*	1.49	1.46	1.39	1.42	1.48	1.51
La/La*	1.38	1.23	1.32	1.26	1.13	1.12
Sm_{SN}/Y_{SN}	1.02	1.04	1.15	1.23	0.734	0.738

Data are normalized using the Post Archean Average Shale (PAAS) values of (Mclennan, 1989).

Eu/Eu* = $Eu_{SN}/(0.67Sm_{SN} + 0.33Tb_{SN})$; Y/Y* = $Y_{SN}/(0.5Dy_{SN} + 0.5Ho_{SN})$; La/La* = $La_{SN}/(3Pr_{SN} - 2Nd_{SN})$ (Robert *et al*[40].). (subscript "SN": normalized to post-Archean Australian Shale, PAAS)



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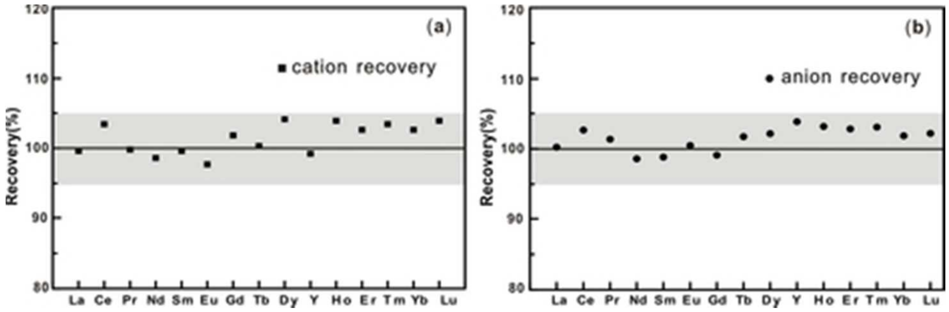

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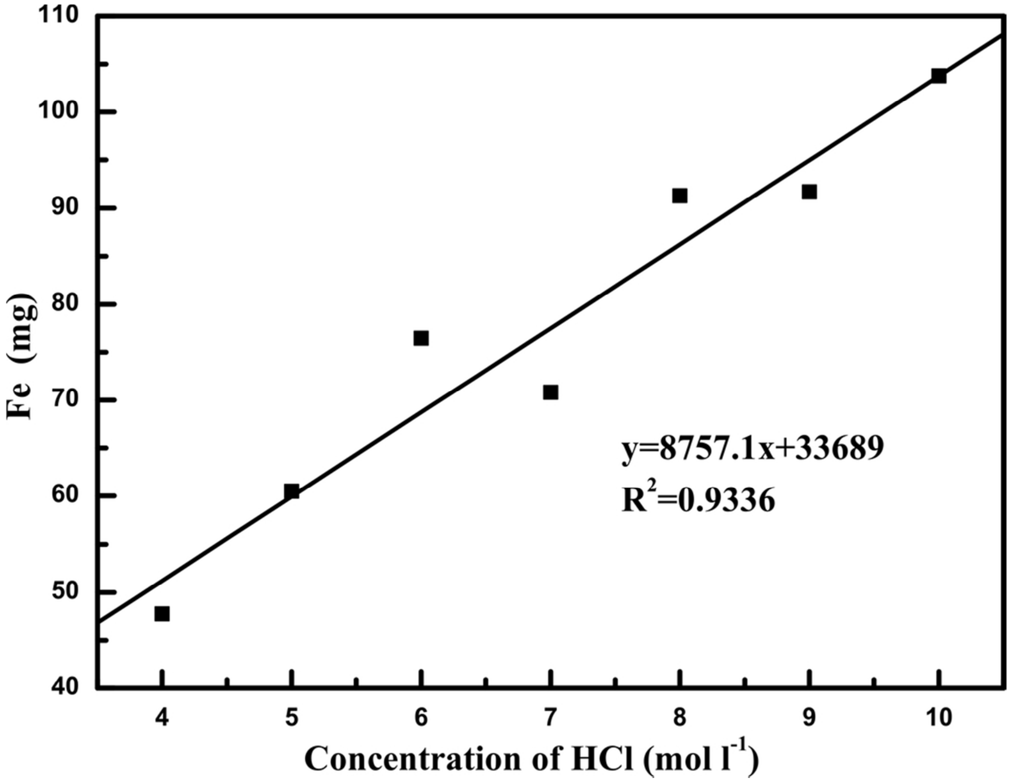

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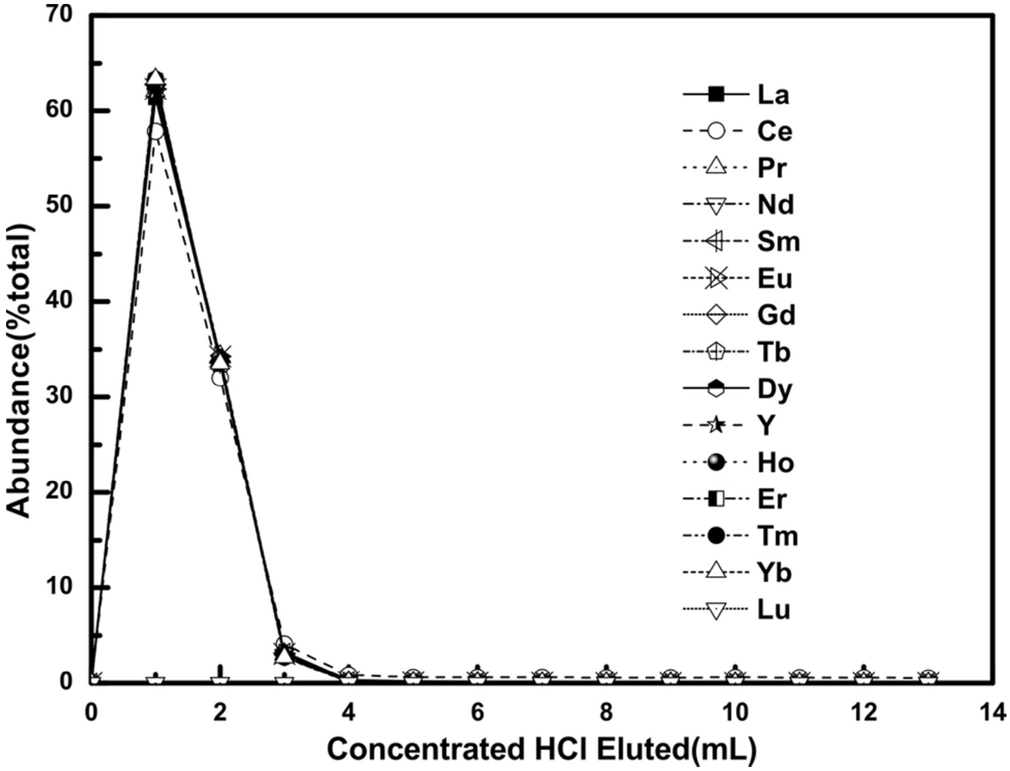

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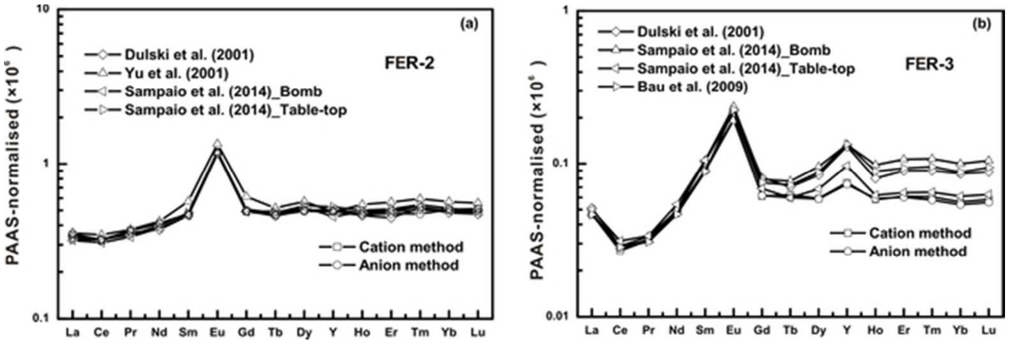

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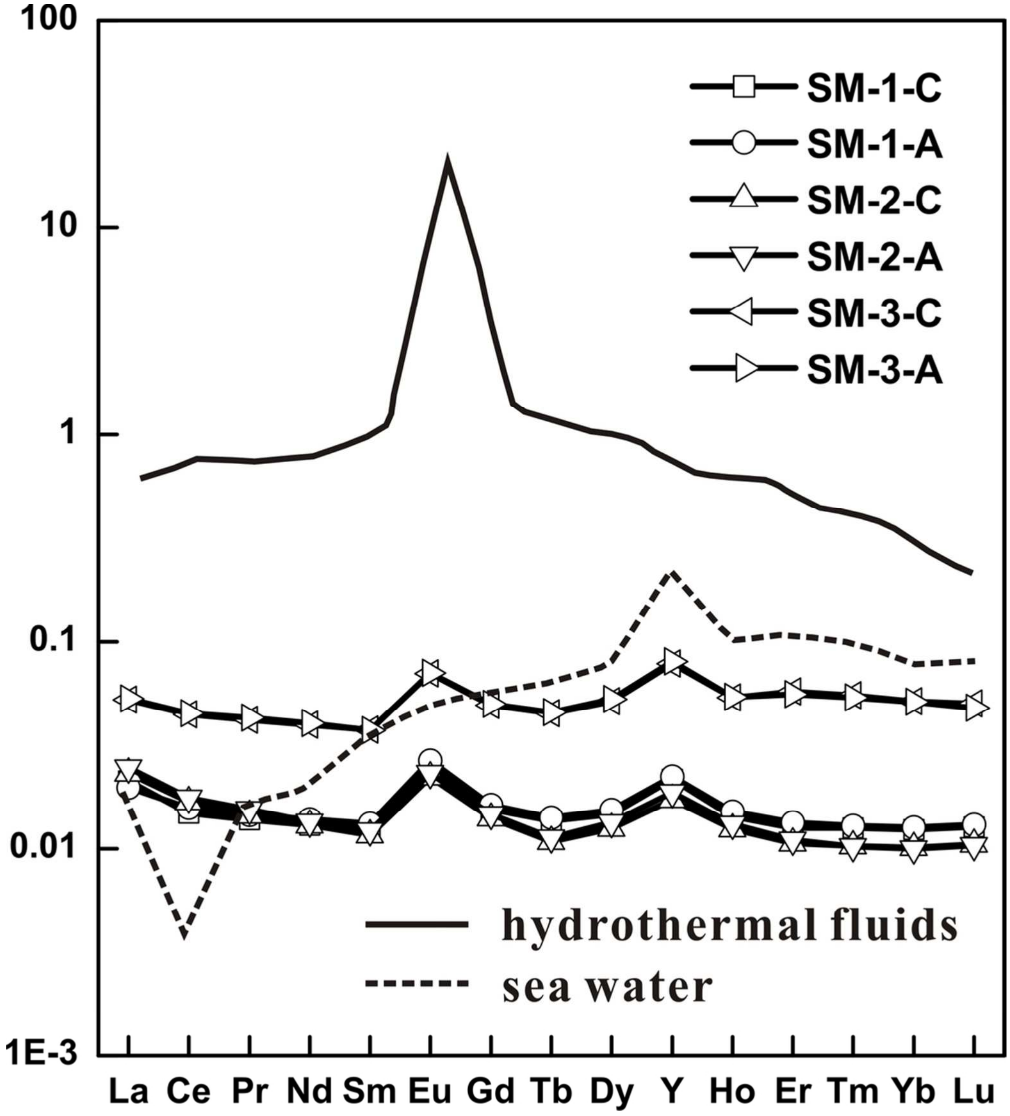

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